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dent W. Lash Miller in the Chair.*

HYPERBASIS.

LECTURE EXPERIMENTS ON SUPERSATURATION, SUPERCOOLING AND SUPERHEATING.

By FRANK B. KENRICK.

The importance of hyperbasis (*Ueberschreitungerscheinungen*) in bringing about thermodynamically "improbable" reactions at the electrodes is now generally recognized, and at the request of the Board of Directors of the Society the illustrated lecture at the present meeting is devoted to this subject. It is hoped that the following notes may make it easy for those who are interested to repeat some of the experiments shown.

APPARATUS.

1. *Projection Cell.* Although lantern cells ("hollow slides") may be obtained commercially, they are often of the wrong shape or size for some special experiment. Moreover, many cells on the market will not stand rapid changes of temperature. The cell described below is free from this objection, and can be easily made or modified in a few minutes.

A glass rod is bent into a U and covered with a rubber tube (*A*, Fig. 1). Near the shorter arm is a second rod, *B*, also covered with rubber tubing. These are clamped, as shown, between two glass plates by means of four strips of wood (1.5 cm. square), *C* and *D*, bolted together at the ends. Hot or cold water, or both, may be led through the tubes, *E* and *F*, the overflow running down between *A* and *B* and being caught in the rectangular tin tray, *G*, on which the lower pair of wooden strips rest and which serves as a stand for the cell. This cell may be made double (see Exp. IV) by clamping, between the same wooden strips, a duplicate cell, in the reverse position, to the right of the cell shown in the diagram. The overflows are thus both on the outside, and do not take up valuable space in the

field of view. If thick glass ($\frac{1}{8}$ -inch) is used, boiling and cold water may be led in alternately without fear of cracking. In the double cell, however, it is safer to use separate glass plates for each half of the cell.

2. *Projection Thermometer.* It may not be generally known that the mercury thread in the capillary of an ordinary milk glass thermometer shows plainly on the screen if the outer protecting tube and scale are removed and the capillary is immersed in water. A lantern thermometer can be prepared in the follow-

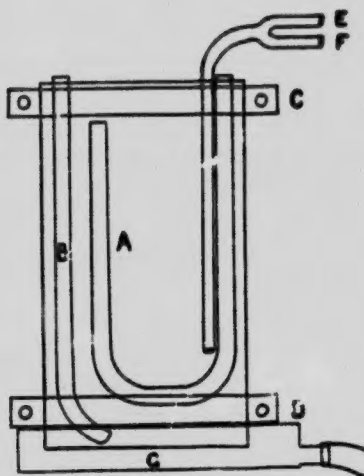


FIG. 1.



FIG. 2.

ing manner, and may be used in the cells described in (1) without monopolising too much of the limited space. The outer tube of an ordinary thermometer (-10° to 360°) is cut off as near the bulb as possible. After cutting off the tip, the capillary is bent back on itself as shown in Fig. 2. The bulb is then warmed with a Bunsen flame, while the tip of the tube is dipping in a vessel of clean mercury. As soon as the mercury column joins the mercury in the vessel the bulb is allowed to cool so as to fill the tube with mercury. The bulb is next warmed in melted paraffin to about 130° to get rid of the excess of mercury, and is finally cooled until the end of the thread has receded a few

centimeters from the tip of tube, whereupon the end is sealed up. This will bring the 100° and 0° marks into the field of view of the lantern. The small quantity of air left in the tube prevents a breaking of the hanging column of mercury. For the scale, a strip of window glass may be etched with hydrofluoric acid and attached to the capillary by cork wedges bound with thread. To economize space, a piece may be cut out of the side of the scale to make room for the thermometer bulb.

3. *Time Measurement.* A very convenient way of indicating time in fractions of a minute is to attach a small plane mirror, about 1 cm. in diameter, to the second-hand of a cheap alarm clock. The clock is held in a retort stand a foot or two behind, and to the side of, the lantern, so that a beam of light from a hole in the side of the lantern house may be reflected back from another mirror to the small mirror on the clock. If the plane of the small mirror is not exactly at right angles to the axis of rotation a spot of light will travel in a circle on the screen, and may be so adjusted that it runs round just outside the illuminated field. The "clock face" may be made either with pieces of paper pinned on the screen, or, if too much of the field is not taken up with apparatus, by the projection of an etched glass plate. To allow easy adjustment, the small mirror may be stuck to a cork impaled on a wire soldered to the second-hand, and bent at right angles to the axis.

4. *Second Pendulum.* A simple metronome for beating seconds can be made from a metal rod four or five inches long, through the middle of which is soldered a stiff wire, the ends of which are pointed and bent down at right angles. These points form bearings which rest on two pieces of metal held in a retort stand. Metal clamps ("bossheads" or "collars", such as are used for fastening rings to stands are attached to the upper and lower ends of the rod and adjusted so that the pendulum beats seconds. The shadow of this pendulum, or of a cardboard pointer attached to it, may be thrown on the screen by a single reflection of a beam of light from the side of the lantern house. No lenses are required either for this or for the clock described in the preceding paragraph.

EXPERIMENTS.

I. Absence of Supersaturation in Solutions of Liquids in Liquids. A good lecture experiment to illustrate this point may be made with a mixture of phenol and water. A flat capillary tube containing water, shaken up with about 20 percent by volume of phenol, is placed alongside the projection thermometer in the lantern cell. When the temperature is gradually raised and lowered the tube becomes suddenly transparent and opaque alternately, at practically the same temperature, as the saturation point is passed. The capillary tube should be about 3 mm. wide by 0.5 mm. thick, inside dimensions. Such tubes may be made by flattening a bulb with a pair of tongs, reheating, and pulling out.

The difficulty of obtaining supersaturated solutions of liquids in liquids has been noted by several observers (Rothmund,¹ Füchtbauer,² Fawcett³). Füchtbauer suggests that dust particles, which are probably amorphous, act as nuclei for liquids and not for crystalline substances. He himself, however, observed that purification of the liquid made very little, if any, difference. Fawcett obtained similar results. It is possible that the cause of the small degree of supersaturation of liquids is connected with the comparatively small surface tension of the interface between liquid and liquid. At any rate, the following calculations in two typical cases, for which data are available, are of interest. Taking the surface energy of the interface gypsum-saturated solution as 550 ergs per sq. cm.,⁴ and assuming arbitrarily the radius of the particles initially formed to be 15 $\mu\mu$ (0.0000015 cm.),⁵ a simple calculation shows that, for equilibrium, the solution would have to be about six times as strong as the normally saturated solution. This is probably well beyond the limit of supersaturation actually reliable. On the other hand, in the case of isobutyric acid and water, the surface energy of whose interface is 1.76 ergs, particles of the acid with a radius

¹ Zeit. phys. Chem., 26, 444 (1898).

² Zeit. phys. Chem., 48, 566 (1904).

³ Proc. Roy. Soc. Canada, 1913.

⁴ Hulett, Zeit. phys. Chem., 37, 404 (1901). A slip in the calculation of this value was corrected by Freundlich, "Capillarchemie," 1909, p. 144, but Freundlich takes Hulett's value for the diameter of the particles instead of the radius. With this additional correction the value is 550.

⁵ 15 $\mu\mu$ is the thickness of the black spot in a soap bubble. This value is also within the limits of the various experimentally determined thicknesses of films of matter which show the properties of the substances in mass.

of 15μ would be in equilibrium with a solution only 0.8 percent stronger than the normally saturated solution. At the ordinary temperature this corresponds to a change of temperature of about 0.5° .^{*} Since it is very difficult to determine accurately the temperatures at which turbidity appears and disappears—the identity of which is the usual criterion for absence of supersaturation—a difference of this order of magnitude might easily escape observation.

II. Superheating of Liquids. It is very easy to superheat liquids in small, clean tubes. When a liquid begins to boil, the ebullition usually takes place quite locally, either at a few fixed points on the walls of the vessel or from particles suspended in the liquid from which streams of bubbles may be seen rising. The smaller the vessel and the smaller the volume of the liquid the less is the chance of the presence of these starting-points for bubbles. It appears, moreover, that there is a gradation in the effectiveness of the nuclei present—i. e., one will cause ebullition when the liquid is slightly superheated, while others will not become effective until the liquid is heated to a higher temperature—for the smaller the tube the higher is the temperature to which the liquid can be heated without boiling. This is in accordance with the law of probability; the nuclei of medium effectiveness are the most abundant, and therefore, on decreasing the size of the tube, the most (and least) effective nuclei are the first to disappear. This may be shown in the projection cell by gradually heating simultaneously three glass tubes (0.7 mm., 1.5 mm. and 3 mm. internal diameter) half filled with ether. The largest tube may be heated to about 60° , when suddenly either all or part of the ether jumps out of the tube. In the second tube the ether does not explode until the temperature has risen many degrees higher, while the smallest tube may often be heated to over 90° without the hyperbasis being relieved, although the ether may be seen to be evaporating with great rapidity at the free surface.

The effect of the insertion of a fine capillary tube, open at the lower end, may be shown in the larger tube of ether, superheated to about 50° . Also the effect of a grain of pipe clay and of a platinum wire may be demonstrated in the same tube. The latter

^{*} Alexjew, Wied. Ann. 28, 305 (1886).

causes a temporary disturbance, but generally loses its effectiveness after a few seconds.

It is interesting to note that, if the same assumption be made as in the previous experiment as to the initial size of the bubbles ($15\ \mu$), and if the surface energy of ether at 90° is taken as 9 ergs,⁷ a calculation of the pressure in the bubbles gives a value of about 12.5 atmospheres. This corresponds to a temperature of about 130° (extrapolated).

III. Linear Rate of Crystallisation. The relation between temperature and linear rate of crystallisation may be shown with melted vanillin. A thin-walled capillary tube about 1 mm. in diameter containing solidified vanillin is immersed in the projection cell to within about 3 cm. of the bottom, and boiling water run through the cell. This melts all the vanillin below the surface of the water, but leaves a quantity of unmelted solid in the upper end of the tube. The water is then cooled to about 75° , and the tube pushed down further into the cell and held in position against the thermometer scale with a cork wedge. At the same time the second pendulum described in paragraph 4 is set in motion. The rate of crystallisation is measured by the number of marks on the thermometer traversed by the edge of the solid during 20 seconds. The temperature of the cell is lowered by about 5° at a time, and successive readings of rate and temperature are taken as the crystallisation proceeds. If the lantern has a vertical attachment the relation between rate and temperature may be plotted on smoked glass and shown on the screen after each measurement. By timing the intervals properly, a complete curve showing the initial increase in rate below the melting point, the interval of constant rate, and the final decrease in rate with falling temperature, may be plotted on the glass before the crystallisation has reached the end of the tube. The measurements cannot be made below about 37° , since spontaneous crystallisation from nuclei begins at this temperature.

IV. Nuclei and Crystallisation. The relation between the number of nuclei and the temperature and duration of supercooling may be shown by Tammann's "exposure and development" method.⁸ A double projecting cell is used, each section

⁷ Ramsay and Shields, *Zeit. phys. Chem.*, 12, 442 (1893).

⁸ *Zeit. phys. Chem.*, 25, 441 (1898).

of which may be heated and cooled rapidly. Vanillin (MP = 81°) is the most satisfactory substance to use for these experiments. A flattened capillary tube, about 2 mm. x 0.5 mm, inside dimensions, is filled with vanillin, melted in one side of the cell in boiling water, quickly transferred to the other half of the cell, at (say) 20° , and "exposed" for a definite number of seconds (say 5), as shown by the shadow of the pendulum, and finally put back quickly into the first cell, which in the meantime has been cooled to a suitable "development" temperature (60°). It is easier to count the nuclei if the tube is put back into the cold half of the cell immediately they begin to appear; this checks the otherwise too rapid growth. The temperature and time of exposure may, of course, be varied.

For these experiments it is convenient to arrange the four tubes conducting hot and cold water to the two halves of the cell so that they pass through four spring pinch-cocks, fixed in a row on a board. By this means the temperatures of the two parts of the cell may be controlled by the four fingers of one hand, thus leaving the other hand free to manipulate the capillary tube.

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